Optimizing Analytical Performance and Extending the Application Range of Thermal Desorption for Monitoring Air Indoors and Inside Vehicle Cabins

Technical Overview

Introduction

Thermal desorption (TD) is a readily automated gas extraction technology based on standard gas chromatography parameters. It provides an efficient, high-sensitivity alternative to conventional solvent extraction. The process of TD involves the extraction of volatile or semivolatile organic compounds from a sorbent or material by heating the sample in a flow of inert gas. The extracted analytes are then transferred in the flow of carrier gas to the analyzer [typically a gas chromatograph (GC) or a gas chromatograph/mass spectrometer (GC/MS)] as a small, discreet, and concentrated volume of vapor. The thermal desorber becomes a multipurpose, standalone GC injector. Concentration factors as high as 10^5 to 10^6 can be achieved using modern systems with analytes collected from tens to hundreds of liters of air being delivered to the analyzer in as little as 200 µL of gas.

Though inherently simple, many factors contribute to the performance and efficiency of the TD process, which determines the ultimate sensitivity and reliability of a TD-based analytical method. These factors include retention efficiency (during sampling/focusing), desorption efficiency, artifacts, band broadening, and analyte/system stability. This overview describes optimization of all of these parameters during the development and validation of TD procedures. Examples of optimum method performance in terms of precision, linearity, and sensitivity are presented. A novel approach to overcoming the traditional one-shot limitation of TD is also described.

Analytical TD — The Process

Analytical TD is a gas-phase introduction technique for vapor-phase analytical systems such as GC and GC/MS. It combines many pre-analytical procedures including sample preparation/collection, selective concentration, analyte extraction, and injection into one labor-saving automated operation. It is used for the measurement of trace volatile organic compounds (VOCs); however, the range of sample types and applications is very diverse:

- Air can be sampled and analyzed online on a semicontinuous basis for real-time studies. Examples include diurnal variation of indoor air pollution, real-time tracer gas studies, etc.
- Building materials and furniture are large contributors to indoor air pollution. The volatile content of solid or liquid samples such as paints or textiles can be measured by weighing the material into empty sampling tubes for extraction and quantitative analysis by direct TD-GC/MS.
- In other cases, vapor phase samples can be collected offline into containers (canisters, bags, etc.) or sorbent tubes. Relevant applications for collection in sorbent tubes include exhaust from materials emission tests, indoor air pollution profiling, studies of building ventilation using tracer gases, and the characterization of odors.

Regardless of the primary sampling device used, volatiles are ultimately swept by the carrier gas into a secondary focusing device inside the thermal desorber where target analytes are selectively retained. Once all the compounds of interest have been transferred to the focusing device and all unwanted volatiles (water, for example) have been swept to vent, the focusing device is thermally desorbed by rapid heating in a reverse flow of inert gas. This process 'injects' target compounds into the analyzer in a tiny, concentrated 'slug' of vapor.

Sampling Options

Containers – Canisters and Bags

Containers, such as passivated canisters or Tedlar™ bags, are the best air sampling option for ultravolatile chemicals such as C2 hydrocarbons. Though expensive, evacuated canisters provide the simplest of all air sampling options with 'grab' sample collection via release of a single valve. However, Tedlar bags offer limited storage stability (<24 hours) for many common VOCs [1]. Canisters are similarly prone to poor recovery of less volatile or more polar species [2] when used for higher concentration atmospheres. Many polar or less volatile species tend to stick to the internal walls of containers and cannot be quantitatively recovered. Humidity can also cause problems. If liquid water condenses inside the container, organic compounds, particularly the more polar species, will partition between the aqueous and vapor phases, giving unreproducible results. While Tedlar bags are typically used only once, canisters can be reused indefinitely. However, they require stringent cleaning by repeated evacuation and purging between uses.

Vapor Sampling onto Sorbent Tubes

While no single sampling method suits all indoor applications, TD sample tubes may provide the most versatile option. Used either empty for desorbing volatiles from materials (see below), or packed with sorbent for retaining vapor-phase organics, they are compatible with all but the most volatile species (for example, acetylene, ethylene, and some freons). Typically, a known volume of air is pulled through the tube at around 50 mL/min using a standard pump. Alternatively, industry-standard steel or coated steel tubes, which have a well-defined, fixed-air gap between the end of the tube and the sorbent sampling surface, can also be used as diffusive (passive) samplers. In this mode, tubes are simply left open at the sampling end, allowing analytes to migrate from the air to the sorbent at a rate controlled by the diffusion gradient according to Fick's first law.

Many of the limiting factors dictating the performance of sorbent tube based air sampling methods (pumped or diffusive) relate to sorbent selection and preparation.

Optimizing Analytical Performance for Sorbent Tube-Based Methods

Sorbent Selection

Sorbent strength – Analytical sensitivity and precision are largely determined by sampling efficiency, desorption efficiency, and the level of interferences (see section on artifacts below). The sorbent(s) selected must be sufficiently strong enough to retain target analytes during sampling/concentration, but weak enough to release them efficiently during the TD phase.

Concentration enhancement potential – Depending on the retentive strength (breakthrough volume) of the sorbent tube selected for the analytes in question, as much as 100–200 L of air can be pumped through a sorbent tube during sampling. During primary (tube) desorption the compounds of interest can be eluted in as little as 100–200 mL of carrier gas and transferred to the focusing trap. Using new, state-of-the-art, fast desorption traps, analytes can subsequently be desorbed from the trap and transferred to the analyzer, splitless, in as little as 200 µL of gas. This produces an overall concentration enhancement of 10^6. Exceptional detection limits can be achieved, even with a conventional Flame Ionization Detector (FID) (Figure 1).

A wide range of sorbents is now commercially available. These can be classified generally as weak, medium, or strong. Less volatile analytes should be trapped on weaker sorbents, while more volatile analytes should be trapped on stronger sorbents. If a wide volatility range of compounds is being monitored, it is often necessary to pack the tube with more than one sorbent material and to arrange them in order of increasing strength, starting from the sampling end. At ambient

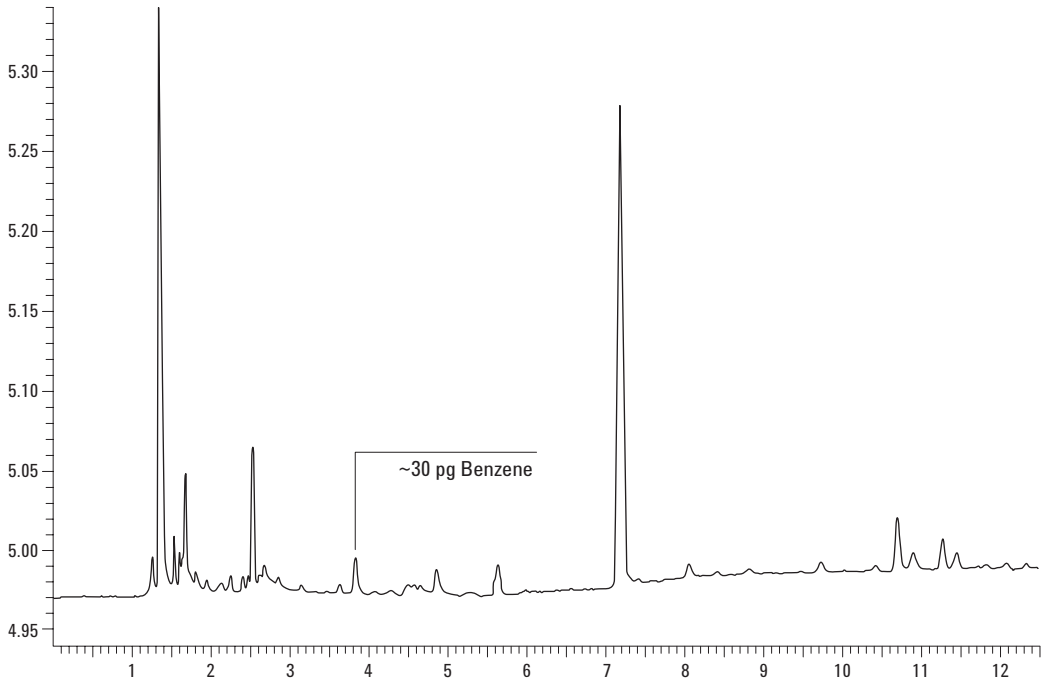

Figure 1. Thirty pg of benzene from a sorbent tube. Equivalent to 10 ppt in 1 L of air.

temperatures, sorbents can be used to retain quantitatively compounds as volatile as vinyl chloride monomer (VCM) and propane. Electrically-cooled sorbent focusing traps can concentrate the most volatile freons and components as volatile as acetylene without additional cooling from liquid cryogen.

Other key considerations when selecting sorbents include:

- **Inertness** – Some sorbents are contaminated by chemically active materials, such as trace metals, from the production process. This is especially true of carbon blacks, many of which derive originally from natural charcoals.
- **Hydrophobicity** – Most common weak and medium strength sorbents are very hydrophobic; their sorbent strength is not compromised even when sampling at high (>90%) humidity. However, most strong sorbents are comprised of some sort of carbonized molecular sieve, and their sorbent strength can be reduced at very high humidity by as much as a factor of 10. If a large amount of water is retained on the tube, this can adversely affect the analysis; however, most modern desorption systems incorporate one or more methods for selectively eliminating water.
- **Artifacts** – Sorbents vary significantly with respect to inherent artifact levels. Some porous polymers, such as the Chromosorb Century series and Poropaks, have relatively high artifacts, with several peaks at 5–10 ng levels. Tenax TA™ is better with minimum levels between 0.1 and 1 ng for well-conditioned materials. Both carbon blacks and carbonized molecular sieves are excellent with respect to inherent artifacts, between 0.01 and 0.1 ng, if well conditioned. However, the carbonized molecular sieves require extended conditioning at steadily increasing temperatures, and when new, can continue to show a high background of inorganic gases for several days.
- **Temperature stability** – Most sorbents, including Tenax TA, are stable up to 350 °C, and many of the carbon sorbents can be taken much higher. Care must be taken with most of the other porous polymers, Chromosorbs and Poropaks, which typically have temperature limits at or below 225 °C. This means that they cannot be packed into mixed-bed tubes with more stable sorbents. If this is done, it is not possible to adequately condition the higher temperature materials without overheating the polymers.

- **Mechanical strength** – Carbon blacks are extremely friable and prone to the formation of fines. Care should be taken not to over compress these sorbents during tube packing and to avoid sharp knocks to the tubes once they are packed. As the carbon packing ages, the formation of fines may increase tube impedance beyond the limit of some pumps. Most other sorbents are mechanically strong, though Tenax TA can have a high percentage of fines when new and may require sieving before use. Generally speaking, recommended mesh sizes for sorbents in standard 4–5 mm bore sampling tubes range from 30–80 mesh. A selection of the most common sorbents and their associated characteristics is presented in Table 1.

Pumped Monitoring/Active Sampling Through Sorbent Tubes

Pumped monitoring is the most versatile sampling option for the compatibility of packed tubes with both single and multibed sorbents. It is specified by a number of international standard methods relating to indoor air. These include prENV 13419 and ISO DIS 16000 for testing emissions from building materials and US EPA Method TO-17, ISO 16017 Pt. 1, and ASTM D6196-97 for general monitoring of VOCs in indoor air. Industry standard ¼-inch od by 3.5-inch long tubes can be sampled efficiently at rates ranging from 10 to 200 mL/min, with the optimum being 50 mL/min [3].

'Universal' tubes – There is no such thing as a universal tube. However, perhaps the most useful combination of sorbents that can be packed into a single tube for pumped monitoring of uncharacterized atmospheres is Tenax TA backed up by Carbopack B™ (Carbograph 1™), in turn backed up by Spherocarb™ (Unicarb™) or Carboxen 1000™. The main limitation of this sorbent combination is that the middle strength carbon black sorbent is not completely inert and may cause degradation of labile analytes such as nitrogen, sulphur-containing compounds, and some monoterpenes. The ultimate 'train' of tubes for monitoring uncharacterized areas consists of three inert Silcosteel tubes connected together in series using inert, nonemitting fittings. The front tube is packed with Tenax TA, the middle one is packed with Chromosorb 106™, and the back one is packed with Unicarb. Whenever using these or any multisorbent combination of tubes, sampling must always take place through the weaker sorbent first. Higher boiling analytes are thus retained by and desorbed from the weak sorbent without coming into contact with the stronger sorbents.

Table 1. Key Features of the Most Common Sorbents

Sorbent	Strength	Features
Tenax TA	Weak	Inert, hydrophobic, individual artifacts below 1 ng, max temperature: 350 °C, sieve to remove fines
Carbograph 1	Weak-Medium	Not inert, hydrophobic, individual artifacts below 0.1 ng, max temperature: >400 °C, prone to fines formation
Chromosorb 106	Medium	Inert, hydrophobic, individual artifacts up to 10 ng, max temperature: 225 °C, precondition to shrink before use
Unicarb/Spherocarb	Strong	Inert, not hydrophobic, individual artifacts below 0.1 ng, max temperature: >350 °C, condition slowly - increasing the temperature stepwise, purge thoroughly to remove O_2 before heating
Carboxen 1000	Ultrastrong	Inert, not hydrophobic, individual artifacts below 0.1 ng, max temperature: >350 °C, condition slowly - increasing the temperature stepwise, purge thoroughly to remove O_2 before heating

Diffusive sampling

Axial samplers – Single-bed, ¼-inch od, 5 mm id stainless steel or Silcosteel sorbent tubes with a 15-mm air gap between the surface of the sorbent and the sampling surface are used as standard for pumped monitoring (see above). However, these tubes were designed as long ago as 1979 [4] to be used as axial format diffusive samplers. The uptake rate of many common solvents is already well validated for these tubes. Diffusive sampling eliminates the expense and relative complexity of sampling pumps and facilitates large-scale air monitoring campaigns at affordable cost. The diffusive sampling rate is a constant function of atmospheric concentration, as predicted by Fick's law, provided the concentration at the surface of the sampler remains at zero (Figure 2).

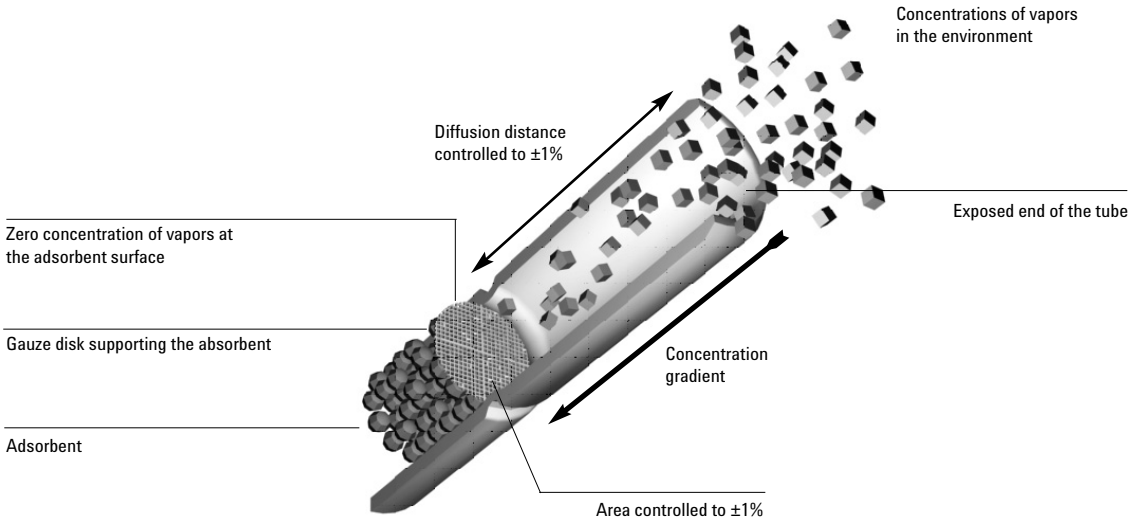

Figure 2. Illustration of diffusive sampling on axial sorbent tubes.

For use as diffusive samplers, the tubes are capped with special diffusion caps at the sampling end and kept sealed at the nonsampling end. The diffusion caps simply have a gauze surface to stop macroparticles from entering the tube and to mask the sorptive surface.

Typical sampling rates on axial diffusive tubes are quoted at around 2 ng/ppm/min (2 pg/ppb/min), which is equivalent to a pumped flow of between 0.5 and 1 mL/min. Standard sorbent tubes may be used in diffusive mode for both short term monitoring (1–8 hours) in high concentration areas and long term (3 days to 4 weeks) monitoring of 'typical' indoor and ambient air.

Radial diffusive samplers – New radial diffusive samplers consist of a sorbent sampling cartridge housed in a porous polymer body; this allows sampling along and around the whole cylindrical surface of the sampler (Figure 3). These devices sample at a rate equivalent to 50–100 mL/min, but saturate quickly. They can only be used for short term 0.5 to 6-hour air monitoring and at ambient/indoor (low ppb) levels. They are a useful complement to the axial diffusive tubes. After sampling, the sorbent cartridge is simply slipped from its porous polymer housing and placed into an empty 'carrier' tube for analysis by TD-GC/MS. The sampling cartridge is an impedance fit inside the middle of the carrier tube to ensure gas passes through the body of the cartridge during desorption. The cartridge may be reused as many times as a standard sorbent tube.

Diffusive sampling is specified by a number of international standard methods relating to indoor air. These include prEN 13528 and ISO 16017 Pt. 2 for general monitoring of VOCs in indoor air and the Dutch standard for ventilation testing using perfluorocarbon tracer gases [5].

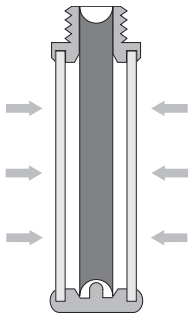

Figure 3. Radial diffusive samplers.

Conditioning and Storage of Sorbent Tubes

To clean them before use, sorbents invariably require stringent conditioning at high temperatures in a flow of inert gas. Many of the porous polymer-type sorbents also require preconditioning in bulk before they are used to pack tubes. This is because as much as 10%–15% of sorbent mass may be lost during the first conditioning cycle. It is rare for any form of solvent washing to be required, but conditions used for tube cleaning should be more stringent (in terms of flow and temperature) than those to be used subsequently for analytical TD.

Conditioned and sampled tubes should be stored using long-term ¼-inch screw caps fitted with combined PTFE ferrules. Tubes capped and stored in this way are reported to be stable for up to 27 months [6], provided the compounds concerned are not chemically active.

Desorption and Analysis

Advice on optimizing and validating the TD and GC/MS analysis process has been described in the literature [7] and is outlined in many of the international standard methods listed above for pumped and diffusive sampling. In summary, analytical desorption temperatures should be kept below those used for tube conditioning with a carrier gas flow of 20-30 mL/min. All air (O_2) should be purged from the tubes before heat is applied, and system flow paths should be kept short, inert, and uniformly heated. TD methods should readily facilitate better than 95% recovery in a single desorption.

The linearity of TD-GC/MS methods should be the same as those achieved using GC/MS with conventional liquid inlets. The precision of TD methods is typically limited to 1%–2% by the manual introduction of standards to sorbent tubes during calibration. However, this is insignificant relative to the overall variability of the complete sampling and analysis procedure for indoor or ambient air. Most standard methods quote this at 15%–30%.

As demanded by international standard methods, TD instrumentation should feature automatic leak testing and tubes that are sealed before and after analysis to maintain data integrity.

SecureTD™ Repeat Analysis for TD

Given its enormous advantages over solvent extraction of adsorbents (in terms of sensitivity, reusable tubes, reproducibility, and environmental acceptability), it is sometimes surprising that TD has not universally replaced solvent extraction for all air monitoring applications. The reason that solvent extraction is still used, especially for some industrial applications, is that more than one analysis can be carried out on each extracted sample. TD, on the other hand, has traditionally been a one-shot technique; once a sample has been thermally desorbed (heated in a flow of inert gas), it is gone. No sample remains for repeat analysis. The latest commercial TD technology overcomes this limitation by offering quantitative re-collection of the split effluent for repeat analysis. In all but the lowest (ppt) level applications, a split can be used. In some cases, when determining the solvent content of coatings or adhesives for example, a large split is often necessary for optimum analytical performance. The latest commercial TD apparatus facilitates quantitative split re-collection for repeat analysis. In these systems, the normal charcoal filter is designed to be the same size as a standard sorbent tube and is easily interchanged. The flowpath leading up to the split point is also uniformly heated and inert. For sample re-collection, the charcoal tube is simply replaced with a conditioned sorbent tube. A steep temperature gradient along the first portion of the re-collection tube ensures good retention efficiency.

The re-collected sample can be archived for analysis by a third party lab or re-analyzed immediately under the same or different analytical conditions as required. Excellent precision can be obtained (Figure 4).

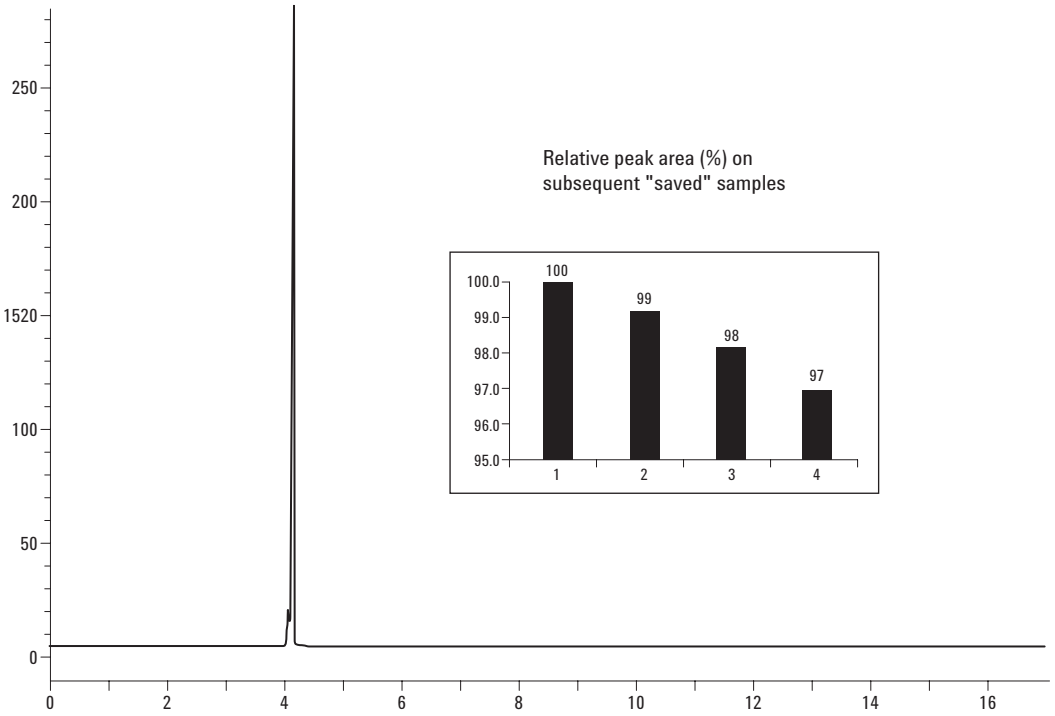

Figure 4. Re-collection and repeat analysis of desorbed toluene.

The Field and Laboratory Emissions Chamber (FLEC)

The FLEC (Figure 5) is a specialized piece of sampling apparatus for testing VOC emissions from construction products and other materials used indoors. It is a simple, portable materials emissions chamber that is shaped like the mouth of a trumpet. It is placed onto the surface of a planar material and air is passed uniformly over the surface. Exhaust gases are collected onto one or two sorbent tubes and then analyzed using standard TD-GC/MS techniques.

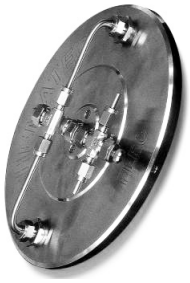

Figure 5. Field and laboratory emission cell (FLEC) for emission testing.

The FLEC complies with Section 2 of the new European standard for testing VOC emissions - prENV 13419. FLEC applications include emissions testing from applied wall coverings, floor coverings, adhesives, sealant materials, paints, and coatings.

Breath Sampling as a Tool for Investigating Biological Exposure

The Bio-VOC Breath Sampler (Figure 6) is a disposable device that collects a 100-mL sample of end-tidal air and transfers it to a sorbent tube [8]. Several breath samples from the same individual can be loaded onto the same sample tube if required. Analysis is typically done by conventional TD-GC/MS.

Figure 6. Monitoring biological exposure via alveolar air collected using the Bio-VOC breath sampler.

Indoor air-related applications for the Bio-VOC Breath sampler include chronic personal exposure monitoring, particularly for individuals living near local emission sources (for example, above a dry cleaning shop).

Direct Desorption

Direct TD provides a convenient and high-sensitivity alternative to purge and trap or solvent extraction for some relatively homogeneous materials. Samples such as powders, film, fibers, granules, resin, or even droplets of liquid can be weighed directly into empty tubes or special PTFE tube inserts.

The sample is then heated in a stream of inert carrier gas that strips volatiles from the sample and transfers them to the focusing trap. In this mode, TD becomes a dynamic headspace procedure.

It is used for complete and quantitative extraction of residual volatiles to determine the solvent or volatile content of a sample. Examples of building materials suitable for this approach include printed polymers/papers, carpet, water based paint, wood varnish, adhesives, etc.

For many quality control and trouble-shooting applications, direct TD eliminates hours of conventional sample preparation. In many cases, a 3-way separation can be achieved. Solids are left in the sample tube and prevented from contaminating the analytical system, and unwanted interferents such as water or ethanol may be eliminated during the focusing process. This leaves only the target organics to be collected in the focusing trap and transferred to the analyzer.

Samples may be weighed directly into empty tubes supported by two glass wool plugs or placed into inert tube inserts such as PTFE liners to prevent contamination of the inner surface of the tube. If complete, quantitative extraction is required, samples should have a relatively high surface area to mass ratio. Examples of such samples include powder, granules, liquid droplets, or fibers. Resins should be smeared inside PTFE inserts or onto glass fiber 'boats' to prevent contamination of the inside of the tube. Similarly, liquids (emulsions, solutions, etc.) can be introduced as droplets on glass wool plugs inside PTFE liners. It is important to make sure the sample does not block the sample

tube; this will stop the gas flow and prevent complete TD. In addition, make sure that the sample is not taken above its decomposition temperature. An example of paint analysis by direct TD-GC/MS is shown in Figure 8.

Summary of Applications for TD in Indoor Air Monitoring

TD methods provide a high sensitivity and robust analytical option for a wide range of indoor air monitoring and related applications. A summary of some key applications is given below, along with useful references. Factors affecting method optimization were described and many key applications relating to indoor air were referenced. A summary of these and other relevant TD applications is listed below with key references:

- Testing VOC emissions from building materials and furnishings [9, 10]
- Indoor air profiling [11]
- Ventilation testing [5]
- VOC content of materials [12]
- Identifying indoor mold/fungal contamination via VOC profiling [13]
- Biological exposure testing [14]
- Real-time air profiling for diurnal variation studies [15]

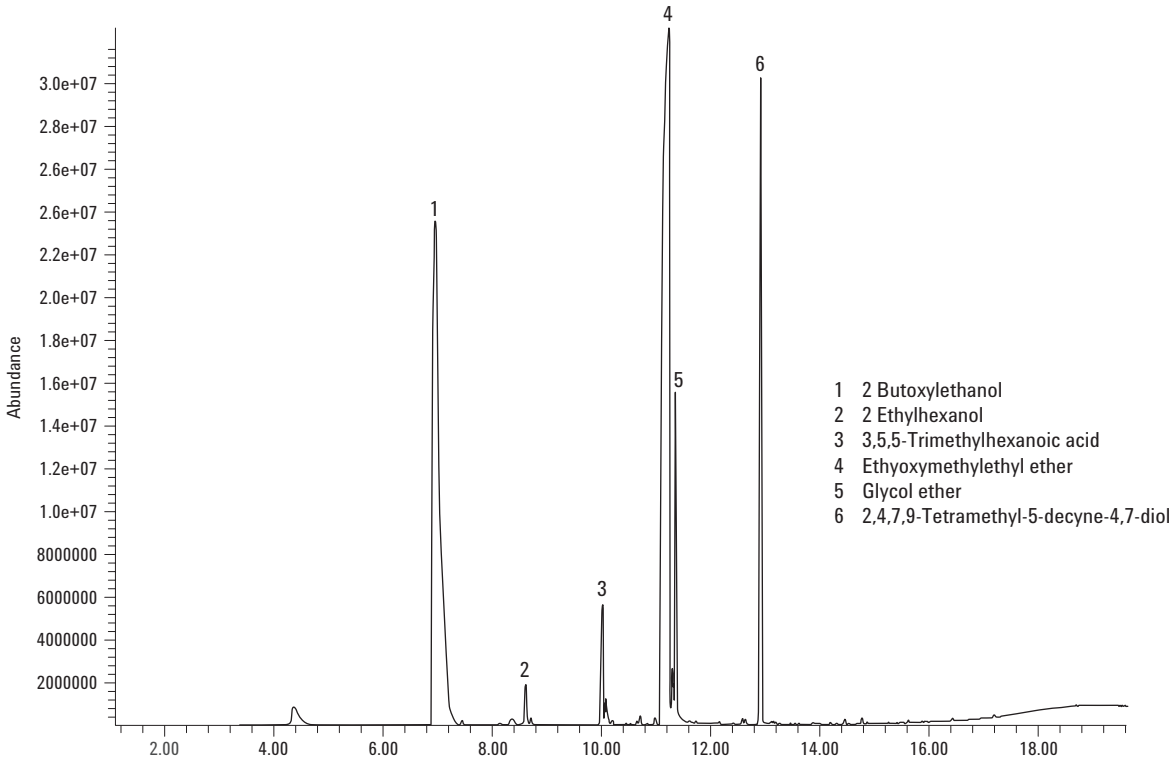

Figure 8. Direct desorption of volatile and semi-volatile organics from paint.

References

1. ASTM; D6399-99a. Standard guide for selecting instruments and methods for measuring air quality in aircraft cabins.
2. Coutant, R.W., and McClenny, W.A. Competitive adsorption effects and the stability of VOC and PVOC in canisters. Proceedings of 1991 USEPA/AWMA International Symposium: Measurement of Toxic and Related Air Pollutants 1991; Vol 1: 382-388.
3. Brown, R.H., and Purnell, C.J. Collection and analysis of trace organic vapor pollutants in ambient atmospheres. The performance of a Tenax-GC adsorbent tube. (1979) *J. of Chrom.* **178**, 79-90.
4. Brown, R.H., Charlton, J., and Saunders, K.J. The development of an improved diffusive sampler. (1981) *Am. Ind. Hyg. Assoc. J.* **42,** 865-869.
5. HJTh Bloemen et al. Ventilation rate and exchange of air in dwellings. Netherlands Nat'l Inst. for Public Health and Environmental Hygiene, with RIVM. 1992 Report.
6. Lindquist, F., and Bakkeren, H. Stability of chlorinated hydrocarbons on Tenax. CEC commissioned report from TNO, the Netherlands, Rpt. No. R90/268, 1990.
7. Woolfenden, E.A. Monitoring VOCs in air using sorbent tubes followed by thermal desorption capillary GC analysis: Summary of data and practical guidelines. (1997) *Journal of Air & Waste Mngmnt Assoc.* **47,** 20-36.
8. Wilson, H.K., and Monster, A.C. New technologies in the use of exhaled breath analysis for biological monitoring. (1999) *Occup Environ. Med.* **56,** 753-757.
9. Wolkoff, P. An emission cell for measurement of volatile organic compounds emitted from building materials for indoor use - the field and laboratory emission cell FLEC. (1996) *Gefahrstoffe-Reinhaltung der Luft* **56,** 151-157.
10. Jensen, B., Wolkoff, P., Wilkins, C.K., and Clausen, P.A. Characterization of linoleum. Part 1. Measurement of VOC by use of FLEC (1995) *Indoor Air* **5**, 38-43.
11. Brown, V.M., Crump, D.R., Gardiner, D., and Yu, C.W.F. Long term diffusive sampling of volatile organic compounds in indoor air. (1993) *Environmental Technology* **14,** 771-777.
12. Monitoring materials and processes for trace level VOCs. Markes International Ltd. Thermal Desorption Technical Support Note 9.
13. Bjurman, J. and Kristensson, J. Volatile production by aspergillus versicolor as a possible cause of odor in houses affected by fungi. (1992) *Mycopathologia*, **118,** 173-178.
14. Wilson, H.K. Breath analysis. Physiological basis and sampling techniques. Scand. J. Work. (1985) *Env. Health*, **12**, 174-192.
15. US EPA, Office of Air Quality Planning and Standards Enhanced ozone monitoring network design and siting criteria guidance document EPA - 450/4-91-033, 1991.

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